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(54) Title: LIQUID CRYSTAL DETERGENT COMPOSITIONS		
(57) Abstract This invention relates to an acidic liquid crystal composition comprising an ethoxylated nonionic surfactant, an aliphatic carboxylic acid, an ethoxylated alkyl ether sulfate surfactant or sodium lauryl sulfate, a weak base, a water-insoluble organic compound selected from perfumes, essential oils and hydrocarbons, a cosurfactant, a magnesium salt and water.		

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LIQUID CRYSTAL DETERGENT COMPOSITIONS

Field of the Invention

This invention relates to an acidic liquid crystal detergent composition. More specifically, it is of an acidic liquid detergent composition in a liquid crystal state which when brought into contact with oily soil is superior to other liquid detergent compositions in detergency and in other physical properties.

Background of the Invention

Liquid aqueous synthetic organic detergent compositions have long been employed for human hair shampoos and as dishwashing detergents for hand washing of dishes (as distinguished from automatic dishwashing machine washing of dishes). Liquid detergent compositions have also been employed as hard surface cleaners, as in pine oil liquids, for cleaning floors and walls. More recently they have proven successful as laundry detergents too, apparently because they are convenient to use, are instantly soluble in wash water, and may be employed in "pre-spotting" applications to facilitate removals of soils and stains from laundry upon subsequent washing. Liquid detergent compositions have comprised anionic, cationic and nonionic surface active agents, builders and adjuvants, including, as adjuvants, lipophilic materials which can act as solvents for lipophilic soils and stains. The various liquid aqueous synthetic organic detergent compositions mentioned serve to emulsify lipophilic materials, including oily soils, in aqueous media, such as wash water, by forming micellar dispersions and emulsions.

Although emulsification is a mechanism of soil removal, it has been only comparatively recently that it was discovered how to make microemulsions which are much more effective than ordinary emulsions in removing lipophilic materials from substrates. Such microemulsions are described in British Patent Specification No. 2,190,681 and in U.S. Patents 5,075,026; 5,076,954 and 5,082,584 and 5,108,643, most of which relate to acidic microemulsions useful for cleaning hard surfaced items, such as bathtubs and sinks which microemulsions are especially effective in removing

soap scum and lime scale from them. However, as in Serial No. 4,919,839 the microemulsions may be essentially neutral and such are also taught to be effective for microemulsifying lipophilic soils from substrates. In U.S. Patent application Serial No. 7/313,664 there is described a light duty microemulsion liquid detergent composition which is useful for washing dishes and removing greasy deposits from them in both neat and diluted forms. Such compositions include complexes of anionic and cationic detergents as surface active components of the microemulsions.

The various microemulsions referred to include a lipophile, which may be a hydrocarbon, a surfactant, which may be an anionic and/or a nonionic detergent(s), a cosurfactant, which may be a poly-lower alkylene glycol lower alkyl ether, e.g., tripropylene glycol monomethyl ether, and water.

Although the manufacture and use of detergent compositions in microemulsion form significantly improved cleaning power and greasy soil removal, compared to the usual emulsions, the present invention improves them still further and also increases the capacity of the detergent compositions to adhere to surfaces to which they have been applied. Thus, they drop or run substantially less than cleaning compositions of "similar" cleaning power which are in microemulsion or normal liquid detergent form. Also, because they form microemulsions with lipophilic soil or stain material spontaneously, with essentially no requirement for addition of any energy, either thermal or mechanical, they are more effective cleaners at room temperature and at higher and lower temperatures that are normally employed in cleaning operations than are ordinary liquid detergents, and are also more effective than detergent compositions in microemulsion form.

The present liquid crystal detergent compositions may be either clear or somewhat cloudy or milky (opalescent) in appearance but both forms thereof are stable on storage and components thereof do not settle out or become ineffective, even on storage at somewhat elevated temperatures for periods as long as six months and up to a year. The presence of the cosurfactant in the liquid crystal detergent compositions helps to make such compositions resist freezing at low temperatures.

In accordance with the present invention an acidic liquid detergent composition, suitable at room temperature or colder, for pre-treating and cleaning materials soiled with lipophilic soil and soap scum, is in liquid crystal form and comprises synthetic organic surface active agent; a cosurfactant, an organic acid, a solvent for the soil, and water. The invention also relates to processes for treating items and materials soiled with soap scum and/or lipophilic soil with compositions of this invention to loosen or remove such soil, by applying to the locus of such soil on such material a soil loosening or removing amount of an invented composition. In another aspect of the invention lipophilic soil is absorbed from the soiled surface into the liquid crystal.

In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls, bathtubs, linoleum or tile floors, washable wall paper, etc.. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic detergents and water-soluble detergent builder salts. In order to achieve comparable cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2,560,839; 3,234,138; 3,350,319; and British Patent No. 1,223,739.

In view of the environmentalist's efforts to reduce phosphate levels in ground water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

However, these prior art all-purpose liquid detergents containing detergent builder salts or other equivalent tend to leave films, spots or streaks on cleaned unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user.

In order to overcome the foregoing disadvantage of the prior art all-purpose liquid, U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a reduced concentration of inorganic phosphate builder salt should be employed.

However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol ether solvent and organic amine as shown in U.S. Patent NO. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

Another approach to formulating hard surfaced or all-purpose liquid detergent composition where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of 25 to 800 Å in a continuous aqueous phase.

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al; and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid detergent compositions. The compositions of this invention

described by Herbots et al. require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

- 5 The following representative prior art patents also relate to liquid detergent cleaning compositions in the form of o/w microemulsions: U.S. Patents Nos. 4,472,291 - Rosario; 4,540,448 - Gauteer et al; 3,723,330 - Sheflin; et al.

 Liquid detergent compositions which include terpenes, such as d-limonene, or other grease-removal solvent, although not disclosed to be in the form of o/w
10 microemulsions, are the subject matter of the following representative patent documents: European Patent Application 0080749; British Patent Specification 1,603,047; and U.S. Patent Nos. 4,414,128 and 4,540,505. For example, U.S. Patent No. 4,414,128 broadly discloses an aqueous liquid detergent composition characterized by, by weight:

- 15 (a) from 1% to 20% of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof;

 (b) from 0.5% to 10% of a mono- or sesquiterpene or mixture thereof, at a weight ratio of (a):(b) being in the range of 5:1 to 1:3; and

- (c) from 0.5% to 20% of a polar solvent having a solubility in water at 15°C in
20 the range of from 0.2% to 10%. Other ingredients present in the formulations disclosed in this patent include from 0.05% to 10% by weight of an alkali metal, ammonium or alkanolammonium soap of a C₁₃-C₂₄ fatty acid; a calcium sequestrant from 0.5% to 13% by weight; non-aqueous solvent, e.g., alcohols and glycol ethers, up to 10% by weight; and hydrotropes, e.g., urea, ethanolamines, salts of lower alkylaryl sulfonates,
25 up to 10% by weight. All of the formulations shown in the Examples of this patent include relatively large amounts of detergent builder salts which are detrimental to surface shine.

 U.S. Patent 5,035,826 teaches liquid crystal compositions but these compositions exhibit thermal stability in the limited temperature range of 19°C to 36°C.

Hard surface cleaners, such as bathroom cleaners and scouring cleansers, have been known for many years. Scouring cleansers normally include a soap or synthetic organic detergent or surface active agent and an abrasive. Such products can scratch relatively soft surfaces and can eventually cause them to appear dull. These products are often ineffective to remove lime scale (usually encrusted calcium and magnesium carbonates) in normal use. Because lime scale can be removed by chemical reactions with acidic media various acidic cleaners have been produced and have met with various degrees of success. In some instances such cleaners have been failures because the acid employed was too strong and damaged the surfaces being cleaned. At other times, the acidic component of the cleaner reacted objectionably with other components of the product which adversely affected the detergent or perfume. Some cleaners required rinsing afterward to avoid leaving objectionable deposits on the cleaned surfaces. As a result of research performed in efforts to overcome the mentioned disadvantages there has recently been made an improved liquid cleaning composition in stable microemulsion form which is an effective cleaner to remove soap scum, lime scale and greasy soils from hard surfaces, such as bathroom surfaces and which does not require rinsing after use. Such a product is described in U.S. Patent 5,076,954 which patent is hereby incorporated by reference. In particular, Example 3 of that application discloses an acidic, clear, oil-in-water microemulsion which is therein described as being successfully employed to clean shower wall tiles of lime scale and soap scum that had adhered to them. Such cleaning was effected by applying the cleaner to the walls followed by wiping or minimal rinsing after which the walls were allowed to dry to a god shine.

The described thickened microemulsion cleaner of U.S. Patent 5,076,954 is effective in removing lime scale and soap scum from hard surfaces and is easy to use, but it has been found that its mixture of acidic agents (succinic, glutaric and adipic acids) could damage the surfaces of some hard fixtures, such as those of materials which are not acid resistant. One of such materials is an enamel that has been extensively employed in Europe as a coating for bathtubs, herein referred to as

European enamel. It has been described as zirconium white enamel or zirconium white powder enamel and has the advantage of being resistant to detergents, which makes it suitable for use on tubs, sinks, shower tiles and bathroom enamelware. However, such enamel is sensitive to acids and is severely damaged by use of the microemulsion
5 acidic cleaner based on the three organic carboxylic acids previously mentioned. This problem was been solved by EPO Patent Application No. 0336878A2, wherein additional acidic materials were incorporated in the cleaner with the organic acids and rather than exacerbating the problem, they prevent harm to such European enamel surfaces by such organic acids. Also, a mixture of such additional acids, phosphonic
10 and phosphoric acids surprisingly further improves the safety of the aqueous cleaner for use on such European enamel surfaces and decreases the cost of the cleaner.

The instant compositions of the present invention allow the cleaning of European enamel surfaces, as well as any other acid resistant surfaces of bathtubs and other bathroom surfaces. The product can be used on various other materials that are
15 especially susceptible to attack by acidic media, such as marble. Additionally, the instant compositions are stable at 25°C for at least 3 months and are shear thinning.

The present invention relates to a thickened acidic aqueous liquid crystal cleaner for bathtubs and other hard surfaced items, which are acid resistant or are of zirconium white enamel, wherein the cleaner has a pH in the range of 1 to 4 and the cleaner
20 removes lime scale, soap scum and greasy soil from surfaces of such items without damaging such surfaces.

U.S. Patent 5,035,826 teaches liquid crystal compositions but these compositions exhibit thermal stability in the limited temperature range of 19°C to 36°C.

Summary of the Invention

25 The present invention provides an improved acidic liquid crystal detergent composition having improved interfacial tension which improves cleaning hard surface in the form of a liquid crystal which is suitable for cleaning hard surfaces such as plastic, vitreous and metal surfaces having a shiny finish, oil stained floors, automotive engines and other engines. More particularly, the improved cleaning compositions

exhibit good grease soil removal properties due to the improved interfacial tensions and leave the cleaned surfaces shiny without the need of or requiring only minimal additional rinsing or wiping. The latter characteristic is evidenced by little or no visible residues on the unrinsed cleaned surfaces and, accordingly, overcomes one of the
5 disadvantages of prior art products.

Surprisingly, these desirable results are accomplished even in the absence of polyphosphate or other inorganic or organic detergent builder salts and also in the complete absence or substantially complete absence of grease-removal solvent.

In one aspect, the invention generally provides a stable, liquid crystal, hard
10 surface cleaning composition especially effective in the removal of oily and greasy oil. The liquid crystal composition includes, on a weight basis:

- (a) 1% to 20% of an ethoxylated alkyl ether sulfate surfactant or sodium lauryl sulfate;
- (b) 1% to 30% of a water-mixable cosurfactant having either limited ability or
15 substantially no ability to dissolve oily or greasy soil;
- (c) 1% to 30% of an ethoxylated nonionic surfactant;
- (d) 1% to 10% of a magnesium salt such as magnesium sulfate heptahydrate and/or magnesium chloride;
- (e) 0.6% to 10% of a perfume, essential oil, or water insoluble hydrocarbon
20 having 6 to 18 carbon atoms;
- (f) 1% to 5% of an aliphatic carboxylic acid having 2 to 10 carbon atoms;
- (g) 0.1% to 3% of weak base; and
- (h) the balance being water, wherein the acidic liquid crystal detergent composition does not contain any sulfonate surfactant, and the liquid detergent
25 composition has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal at a temperature of 20°C to 40°C at a strain of 0.1% to 5% second as measured on a Carr-Med CS Rheometer and is thermally stable and exist as a liquid crystal in the temperature range from 8°C to 43°C, more preferably 4°C to 43°C.

Detailed Description of the Invention

The present invention relates to a stable acidic liquid crystal detergent composition comprising by weight: 1% to 15% of an ethoxylated alkyl ether sulfate surfactant, 1% to 30% of a cosurfactant, 1% to 30% of an ethoxylated nonionic surfactant, 0.6% to 10% of a water insoluble hydrocarbon, essential oil or a perfume, 1% to 5% of an aliphatic carboxylic acid, 0.1% to 3% of weak base, and the balance being water, wherein the acidic liquid crystal composition does not contain any sulfonate surfactant, and the liquid detergent composition has a storage modulus equal to or higher than one Pascal (1 Newton/sq.m.), more preferably higher than 10 Pascal at a temperature of 20°C to 40°C at a strain of 0.1% to 5% second as measured on a Carr-Med CS Rheometer and is thermally stable and exist as a clear liquid crystal in the temperature range from 8°C to 43°C, more preferably 4°C to 43°C.

According to the present invention, the role of the water insoluble hydrocarbon can be provided by a non-water-soluble perfume. Typically, in aqueous based compositions the presence of a solubilizers, such as alkali metal lower alkyl aryl sulfonate hydrotrope, triethanolamine, urea, etc., is required for perfume dissolution, especially at perfume levels of 1% and higher, since perfumes are generally a mixture of fragrant essential oils and aromatic compounds which are generally not water-soluble.

As used herein and in the appended claims the term "perfume" is used in its ordinary sense to refer to and include any non-water soluble fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flower, herb, blossom or plant), artificial (i.e., mixture of natural oils or oil constituents) and synthetically produced substance) odoriferous substances. Typically, perfumes are complex mixtures of blends of various organic compounds such as alcohols, aldehydes, ethers, aromatic compounds and varying amounts of essential oils (e.g., terpenes) such as from 0% to 80%, usually from 10% to 70% by weight, the essential oils themselves being volatile odoriferous compounds and also serving to dissolve the other components of the perfume.

Quite surprisingly although the perfume is not, per se, a solvent for greasy or oily soil, --even though some perfumes may, in fact, contain as much as 80% of terpenes which are known as good grease solvents -- the inventive compositions in dilute form have the capacity to solubilize up to 10 times or more of the weight of the perfume of
5 oily and greasy soil, which is removed or loosened from the hard surface by virtue of the action of the anionic and nonionic surfactants, said soil being taken up into the oil phase of the o/w microemulsion.

In the present invention the precise composition of the perfume is of no particular consequence to cleaning performance so long as it meets the criteria of water
10 immiscibility and having a pleasing odor. Naturally, of course, especially for cleaning compositions intended for use in the home, the perfume, as well as all other ingredients, should be cosmetically acceptable, i.e., non-toxic, hypoallergenic, etc.

The hydrocarbon such as a perfume is present in the liquid crystal composition in an amount of from 0.6% to 10% by weight, preferably from 0.8% to 8% by weight,
15 especially preferably from 1% to 6% by weight. If the amount of hydrocarbon (perfume) is less than 0.6% by weight it becomes difficult to form the liquid crystal. If the hydrocarbon (perfume) is added in amounts more than 10% by weight, the cost is increased without any additional cleaning benefit and, in fact, with some diminishing of cleaning performance insofar as the total amount of greasy or oily soil which can be
20 taken up in the oil phase of the microemulsion will decrease proportionately.

Furthermore, although superior grease removal performance will be achieved for perfume compositions not containing any terpene solvents, it is apparently difficult for perfumers to formulate sufficiently inexpensive perfume compositions for products of this type (i.e., very cost sensitive consumer-type products) which includes less than
25 20%, usually less than 30%, of such terpene solvents.

Thus, merely as a practical matter, based on economic consideration, the liquid crystal cleaning compositions of the present invention may often include as much as 0.2% to 7% by weight, based on the total composition, of terpene solvents introduced thereunto via the perfume component. However, even when the amount of terpene

solvent in the cleaning formulation is less than 1.5% by weight, such as up to 0.6% by weight or 0.4% by weight or less, satisfactory grease removal and oil removal capacity is provided by the inventive compositions.

In place of the perfume in either the microemulsion composition or the all purpose hard surface cleaning composition at the same previously defined concentrations that the perfume was used in either the microemulsion or the all purpose hard surface cleaning composition one can employ an essential oil or a water insoluble organic compound such as a water insoluble hydrocarbon having 6 to 18 carbon such as a paraffin or isoparaffin such as isoparH, isodecane, alpha-pinene, beta-pinene, decanol and terpineol.

Suitable essential oils are selected from the group consisting of: Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Borneol Flakes (China), Camphor oil, White, Camphor powder synthetic technical, Cananga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Coriander (Russia), Coumarin 69°C (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanilin, Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin, Isobornyl acetate, Isolongifolene, Juniper berry oil, L-methyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals, Methyl cedryl ketone, Methyl chavicol, Methyl salicylate, Musk ambrette, Musk ketone, Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol, Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), Wintergreen

The nonionic surfactant is present in amounts of 1% to 30%, preferably 3% to 18% by weight of the liquid crystal composition and provides superior performance in the removal of oily soil and mildness to human skin.

The water soluble ethoxylated nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates and secondary aliphatic alcohol ethoxylates. The length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

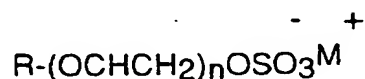
The nonionic surfactant class includes the condensation products of a higher alcohol (e.g., an alkanol containing 8 to 16 carbon atoms in a straight or branched chain configuration) condensed with 4 to 20 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with 16 moles of ethylene oxide (EO), tridecanol condensed with 6 to moles of EO, myristyl alcohol condensed with 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either 6 moles of EO per mole of total alcohol or 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing 9-15 carbon atoms, such as C₉-C₁₁ alkanol condensed with 4 to 10 moles of ethylene oxide (Neodol 91-8), C₁₂-₁₃ alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C₁₂-₁₅ alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C₁₄-₁₅ alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 7 contain less than 4 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the

foregoing type are C₁₁-C₁₅ secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

The anionic surfactants which may be used in the detergent of this invention are water soluble salts and include the sodium, potassium, ammonium, triethanolamine and
 5 ethanolammonium salts of an C₈-18 ethoxylated alkyl ether sulfate surfactants which have the structure:



wherein n is 0 (if n = 0 then it is sodium lauryl sulfate [SLS]) to 5 and R is an alkyl group
 10 having 8 to 18 carbon atoms, more preferably 12 to 15 and natural cuts, for example, C₁₂-14; C₁₂-15 and M is an ammonium cation or a metal cation, most preferably sodium. The ethoxylated alkyl ether sulfate is present in the composition at a concentration of 1% to 20% by weight, more preferably 2% to 15% by weight.

The ethoxylated alkyl ether sulfate may be made by sulfating the condensation
 15 product of ethylene oxide and C₈-10 alkanol, and neutralizing the resultant product. The ethoxylated alkyl ether sulfates differ from one another in the number of carbon atoms in the alcohols and in the number of moles of ethylene oxide reacted with one mole of such alcohol. Preferred ethoxylated alkyl ether polyethenoxy sulfates contain 12 to 15 carbon atoms in the alcohols and in the alkyl groups thereof, e.g., sodium
 20 myristyl (3 EO) sulfate.

Ethoxylated C₈-18 alkylphenyl ether sulfates containing from 2 to 6 moles of ethylene oxide in the molecule are also suitable for use in the invention compositions. These detergents can be prepared by reacting an alkyl phenol with 2 to 6 moles of ethylene oxide and sulfating and neutralizing the resultant ethoxylated alkylphenol. The
 25 concentration of the ethoxylated alkyl ether sulfate surfactant is 1 to 8 wt. %.

The major class of compounds found to provide highly suitable cosurfactants for the microemulsion over temperature ranges extending from 5°C to 43°C for instance are glycerol, ethylene glycol, water-soluble polyethylene glycols having a molecular weight of 300 to 1000, polypropylene glycol of the formula HO(CH₂CHCH₂O)_nH

wherein n is a number from 2 to 18, mixtures of polyethylene glycol and polypropyl glycol (Synalox) and mono C₁-C₆ alkyl ethers and esters of ethylene glycol and propylene glycol having the structural formulas R(X)_nOH and R₁(X)_nOH wherein R is C₁-C₆ alkyl group, R₁ is C₂-C₄ acyl group, X is (OCH₂CH₂) or (OCH₂(CH₃)CH) and n is a number from 1 to 4, diethylene glycol, triethylene glycol, an alkyl lactate, wherein the alkyl group has 1 to 6 carbon atoms, 1 methoxy-2-propanol, 1 methoxy-3-propanol, and 1 methoxy 2-, 3- or 4-butanol.

Representative members of the polypropylene glycol include dipropylene glycol and polypropylene glycol having a molecular weight of 200 to 1000, e.g., polypropylene glycol 400. Other satisfactory glycol ethers are ethylene glycol monobutyl ether (butyl cellosolve), diethylene glycol monobutyl ether (butyl carbitol), triethylene glycol monobutyl ether, mono, di, tri propylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, mono, di, tripropylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, propylene glycol tertiary butyl ether, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monopropyl ether, ethylene glycol monopentyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monopentyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monopentyl ether, triethylene glycol monohexyl ether, mono, di, tripropylene glycol monoethyl ether, mono, di tripropylene glycol monopropyl ether, mono, di, tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monohexyl ether, mono, di, tributylene glycol mono methyl ether, mono, di, tributylene glycol monoethyl ether, mono, di, tributylene glycol monopropyl ether, mono, di, tributylene glycol monobutyl ether, mono, di, tributylene glycol monopentyl ether and mono, di, tributylene glycol monohexyl ether, ethylene glycol monoacetate and dipropylene glycol propionate. Tripropylene glycol n-butyl ether is the preferred cosurfactant because of its hydrophobic character.

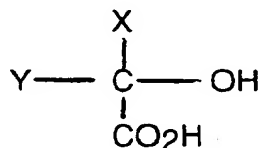
The amount of cosurfactant required to stabilize the liquid crystal compositions will, of course, depend on such factors as the surface tension characteristics of the cosurfactant, the type and amounts of the primary surfactants and perfumes, and the type and amounts of any other additional ingredients which may be present in the composition and which have an influence on the thermodynamic factors enumerated above. Generally, amounts of cosurfactant used in the liquid crystal composition is in the range of from 1% to 30%, preferably from 2% to 20%, especially preferably from 3% to 16%, by weight provide stable liquid crystal composition for the above-described levels of primary surfactants and perfume and any other additional ingredients as described below.

The aliphatic carboxylic acid having 2 to 10 carbon atoms is present in the composition at a concentration of 1 wt. % to 5 wt. %, more preferably 1.25 wt. % to 4 wt. %.

Representative members of the aliphatic carboxylic acids include C₃-C₆ alkyl and alkenyl monobasic acids such as acrylic acid and propionic acid and dibasic acids having 2 to 10 carbon atoms such as glutaric acid and mixtures of glutaric acid with adipic acid and succinic acid, as well as mixtures of the foregoing acids. Generally, weight ratios of adipic acid: glutaric acid: succinic acid is 1-3:1-8:1-5, preferably 1-2:1-6:1-3, such as 1:1:1, 1:2:1, 2:2:1, 1:2:1.5, 1:2:2, 2:3:2, etc. can be used with equally good results.

Of the dicarboxylic acids group, which includes those of 2 to 10 carbon atoms, from oxalic acid through sebacic acid suberic, azelaic and sebacic acids are of lower solubilities and therefore are not as useful in the present emulsions as the other dibasic aliphatic fatty acids, all of which are preferably saturated and straight chained.. Oxalic and malonic acids, although useful as reducing agents too, may be too strong for delicate hard surface cleaning. Preferred such dibasic acids are those of the middle portion of the 2 to 10 carbon atom acid range, succinic, glutaric, adipic and pimelic acids, especially the first three thereof, which fortunately are available commercially, in mixture. Citric acid can also be employed as the acid.

The preferred aliphatic carboxylic acid is an alpha hydroxy aliphatic acid which is strong enough to lower the pH of the microemulsion to one in the range of one to four. Various such carboxylic acids can perform this function but those which have been found effectively to remove soap scum and lime scale from bathroom surfaces best, while still not destabilizing the emulsion, are alpha hydroxy aliphatic acids having the structure:

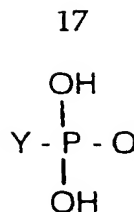


- 10 wherein Y is selected from the group consisting of hydroxy or a COOH group and X is (CH₂)_nW, wherein W is selected from the group consisting of CH₃ or COOH and n is 0, 1, or 2. Preferred alpha hydroxy aliphatic acids are citric acid, lactic acid and malic acid, wherein a mixture of lactic acid and malic acid is preferred, wherein the weight ratio of lactic acid to malic acid is preferred to be 5:1 to 1:1, more preferably 4:1 to 1:1.
- 15 The at least one alpha hydroxy aliphatic acid is incorporated in the composition in an amount of 1 to 9 wt. %, more preferably 2 to 7 wt. %.

The alpha hydroxy aliphatic acid, after being incorporated in the acidic emulsion, may be partially neutralized to produce effectiveness, with safety.

- 20 Phosphoric acid can be used at a concentration of 0 to 1 wt. % and is one of the additional acids that helps to protect acid-sensitive surfaces being cleaned with the present emulsion cleaner. Being a tribasic acid, it too may be partially neutralized to obtain an emulsion pH in the desired range. For example. It may be partially neutralized to the biphosphate, e.g., Na₂H₂PO₄, or NH₄H₂PO₄.

- 25 Phosphonic acid used at a concentration of 0 to 1 wt. % can also be used for protecting acid-sensitive surfaces from the dissolving action of the dicarboxylic acids of the present thickened emulsions, apparently exists only theoretically, but its derivatives are stable and are useful in the practice of the present invention. Such are considered to be phosphonic acids as that term is used in this specification. The phosphonic acids are of the structure.



wherein Y is any suitable substituent, but preferably Y is alkylamino or N-substituted alkylamino. For example, a preferred phosphonic acid component of the present thickened acidic emulsions is aminotris (methylenephosphonic) acid which is of the formula $\text{N}(\text{CH}_2\text{PH}_x\text{O}_3)$. Among other useful phosphonic acids are ethylene diamine tetra-(methylenephosphonic) acid, hexamethylenediamine tetra-(methylenephosphonic) acid, and diethylenetriamine penta-(methylenephosphonic) acid. Such class of compounds may be described as aminoalkylenephosphonic acids containing in the ranges of 1 to 3 amino nitrogen, 3 or 4 lower alkylenephosphonic acid groups in which the lower alkylene is of 1 or 2 carbon atoms, and 0 to 2 alkylene groups of 2 to 6 carbon atoms each, which alkylene(s) is/are present and join amino nitrogen when a plurality of such amino nitrogen is present in the aminoalkylenephosphonic acid. It has been found that such aminoalkylenephosphonic acids, which also may be partially neutralized at the desired pH of the microemulsion cleaner, are of desired stabilizing and protecting effect in the invented cleaner, especially when present with phosphate acid, preventing harmful attacks on European enamel surfaces by the diacid(s) components of the cleaner. Usually the phosphorus acid salts, if present, will be mono-

salts of each of the phosphoric and/or phosphonic acid groups present.

The liquid crystal composition contains a weak base such as diethanolamine or triethanol amine at a concentration of 0.1 wt. % to 2 wt. %. The weak base is employed in the composition to adjust the pH of the composition.

The instant composition contains 0.5 to 8 wt. %, more preferably 1 to 6 wt. % of a magnesium salt such as magnesium chloride and/or magnesium sulfate heptahydrate and mixtures thereof.

The ability to formulate neutral and acidic products without builders which have grease removal capacities is a feature of the present invention because the prior art o/w microemulsion formulations most usually are highly alkaline or highly built or both.

In addition to their excellent capacity for cleaning greasy and oily soils, the low pH liquid crystal formulations also exhibit excellent cleaning performance and removal of soap scum and lime scale in neat (undiluted) as well as in diluted usage.

The final essential ingredient in the inventive acidic liquid crystal compositions having improved interfacial tension properties is water. The proportion of water in the liquid crystal detergent composition generally is in the range of 20% to 97%, preferably 70% to 97% by weight.

A composition of this invention is in a liquid crystal state when it is of lyotropic structure, is transparent or slightly turbid (opalescent) but not opaque, and has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal and most preferably higher than 20 Pascal and when measured at a temperature of 20 to 40°C, at a frequency of ten radians per second and at a strain of 0.1 to 5%. The rheological behavior of the compositions of this invention were measured at 25°C by means of a Carri-Med CS Rheometer. In making the measurement, a cone and plate are used at a cone angle of 2 degrees: 0 minutes: 0 seconds with a cone diameter of 6.0 cm, measurement system gap of 52.0 micro m and a measurement system inertia of 17.02 micro Nm sec⁻².

To make the liquid crystal compositions of the invention is relatively simple because they tend to form spontaneously with little need for the addition of energy to promote transformation to the liquid crystal state. However, to promote uniformity of the composition mixing will normally be undertaken and it has been found desirable first to mix the surfactants and cosurfactant with the water, followed by admixing of the lipophilic component, usually a hydrocarbon (but esters or mixtures of hydrocarbons and esters may also be employed). It is not necessary to employ heat and most mixings are preferably carried out at room temperature (20-25°C).

The invented compositions may be applied to such surfaces by pouring onto them, by application with a cloth or sponge, or by various other contacting means but it is preferred to apply them in the form of a spray by spraying them onto the substrate from a hand or finger pressure operated sprayer or squeeze bottle. Such application

may be onto hard surfaces, such as dishes, walls or floors, from which lipophilic (usually greasy or oily) soil is to be removed, or may be onto fabrics, such as laundry, which has previously been stained with lipophilic soils, such as motor oil. The invented compositions may be used as detergents and as such may be employed in the same manner in which liquid detergents are normally utilized in dishwashing, floor and wall cleaning and laundering, but it is preferred that they be employed as pre-spotting agents too, in which applications they are found to be extremely useful in loosening the adhesions of lipophilic soils to substrates, thereby promoting much easier cleaning with application of more of the same invented detergent compositions or by applications of different commercial detergent compositions, in liquid, bar or particulate forms.

The various advantages of the invention have already been set forth in some detail and will not be repeated here. However, it will be reiterated that the invention relates to the important discovery that effective liquid detergent compositions can be made in the liquid crystal state and that because they are in such state they are especially effective in removing lipophilic soils from substrates and also are effective in removing from substrates non-lipophilic materials. Such desirable properties of the liquid crystal detergent compositions of this invention make them ideal for use as pre-spotting agents and detergents for them ideal for use as pre-spotting agents and detergents for removing hard-to-remove soils from substrates in various hard and soft surface cleaning operations.

The following examples illustrate but do not limit the invention. Unless otherwise indicated, all parts in these examples, in the specification and in the appended claims are by weight and all temperature are in °C.

Example I

The following formulas (wt. %) were made at 25°C by simple mixing.

	A	B	C	D
NaAEOS (2EO)	12	12	6	12
91-5 Dobanol	3	3	6	3
Tripropylene glycol n-butyl ether	12	12	12	12
d-Limonene	4	4	4	4
MgSO ₄ ·7H ₂ O	0.98	0.98	0.48	0.98
Citric acid		3	3	1
Diethanolamine		1	1	0.33
Water	Bal.	Bal.	Bal.	Bal.
Thermal stability °C				
Cleaning easiness index on soap scum				
proto A vs. AME 1:1	0.22		-	-
proto B vs. AME 1:1		0.39		
proto A vs. Gel bath	-0.05			
proto B vs. Gel bath		0.14		
proto A vs. B	-0.26			
proto B vs A		0.21		
proto A vs Mr. Proper ultra bath	-0.71			
proto B vs Mr. Proper ultra bath		0.36		
pH	6.35	3	-	-

The cleaning easiness index is expressed as:

5 [1-(strokes number A.PROTO)/strokes number expert bathroom products)]

If strokes number proto = strokes number ref., then the index is 0 (cleaning equivalence between prototype and reference).

If strokes number proto > strokes number ref. then the index is characterised by a negative value (the more negative the index, the less efficient the prototype).

10 If strokes number proto < strokes number ref. then the index is characterised by a positive value (the more positive the index, the more efficient the prototype).

The soap scum is generated by direct spraying of Oleate Na and and stoichiometric quantity of calcium chloride on ceramic tile.

The cleaning easiness index of A vs different references was calculated by
15 indirect comparison between the neutral proto (A) and the references. In other words, A and references were not directly evaluated in the same tile.

The formula of the gel bath is:

	<u>Wt. %</u>
Xanthan gum	5.0
Paraffin sulfonate	4.0
5 LF400 Plurafac nonionic	3.0
H ₃ PO ₄ (85%)	0.26
Amino trimethyl phosphonic acid	0.05
Perfume	0.75
Water	Balance

10 The formula of Ajax AME 1:1 is the same formula as the gel bath except there is no xanthan gum and in there is an addition 1.5 wt. % of MgSO₄·7H₂O.

The invention has been described with respect to various embodiments and illustrations of it but is not to be considered as limited to these because it is evident that one of skill in the art with the present specification before him or her will be able to
15 utilize substitutes and equivalents without departing from the invention.

What is Claimed is:

1. An acidic liquid crystal detergent composition which comprises by weight:
 - (a) 1% to 30% of an ethoxylated nonionic surfactant containing ethylene oxide groups;
 - 5 (b) 1% to 15% of an aliphatic carboxylic acid;
 - (c) 1% to 20% of a water soluble salt of an ethoxylated C8-18 alkyl ether sulfate surfactant or sodium lauryl sulfate;
 - (d) 0.1 to 2% of a weak base;
 - (e) 0.6% to 10% of a water insoluble organic compound selected from the
 - 10 group consisting of perfumes, essential oils and water insoluble hydrocarbons;
 - (f) 1% to 30% of a cosurfactant;
 - (g) 1% to 10% of a magnesium salt; and
 - (h) the balance being water, said liquid crystal detergent composition having a storage modulus measured at a temperature between 20°C to 40°C, at a strain of
 - 15 0.1% to 5% and a frequency of 10 radians/second of at least one Pascal and is one phase at a temperature of 8°C to 45°C.
2. The composition of Claim 1, wherein said nonionic surfactant is a condensation product of one mole of a higher fatty alcohol having 9 to 11 carbon atoms with 2 to 5 moles of said ethylene oxide groups.
- 20 3. The composition of Claim 2 wherein said water soluble salt of said ethoxylated C8-18 alkyl ether sulfate surfactant has a cation selected from the group consisting of sodium, potassium and ammonium.
4. The composition of Claim 3 wherein said aliphatic carboxylic acid is citric acid.
- 25 5. The composition of Claim 3, wherein said water insoluble hydrocarbon is selected from the group consisting of d-limonene, alpha-terpineol, alpha-pinene, and beta pinene and mixtures thereof.
6. The composition of Claim 1, wherein said carboxylic acid is citric acid.

7. A process for removing any one or more of lime scale, soap scum, and greasy soil from bathtubs or other hard surfaced items, which are acid resistant or are of zirconium white enamel, which comprises applying to such a surface a composition in accordance with Claim 1 and removing such composition and the lime scale and/or
- 5 soap scum and/or greasy soil from such surface.

INTERNATIONAL SEARCH REPORT

 Intr. National Application No
 PCT/US 97/04065

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 6	C11D17/00 C11D3/43	C11D1/83 C09K19/00
C11D3/20	C11D3/16	C11D3/30
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
IPC 6 C11D C09K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 035 826 A (DURBUT PATRICK J ET AL) 30 July 1991 cited in the application see the entire document ---	1-7
A	EP 0 637 629 A (COLGATE PALMOLIVE CO) 8 February 1995 see page 6, line 1 - line 19; claims 1-16; examples 1-6 ---	1-7
A	EP 0 125 711 A (UNILEVER NV ;UNILEVER PLC (GB)) 21 November 1984 see page 3, line 17 - page 4, line 33; page 8, line 20 - page 9, line 18; examples 1-12; claims 1-4 ---	1-7
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
1 July 1997		23. 07. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016		Authorized officer Ainscow, J

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/04065

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 05757 A (UNILEVER PLC ;UNILEVER NV (NL)) 17 March 1994 see page 9, line 24 - page 14, line 16; page 16, line 22 - page 17, line 4; examples 1-26; claims 1-18 ---	1-7
A	US 5 403 515 A (INSTONE TERRY ET AL) 4 April 1995 see the entire document ---	1-7
A	EP 0 336 878 A (COLGATE PALMOLIVE CO) 11 October 1989 cited in the application see the entire document -----	1-7

INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 97/04065

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5035826 A	30-07-91	AT 145936 T	15-12-96
		AU 630232 B	22-10-92
		AU 6304090 A	28-03-91
		CA 2025956 A	23-03-91
		DE 69029306 D	16-01-97
		EP 0418986 A	27-03-91
		ES 2097132 T	01-04-97
		GR 1000680 B	08-10-92
		HU 212246 B	29-04-96
		JP 3207799 A	11-09-91
		NO 177908 B	04-09-95
		US 5523013 A	04-06-96
EP 0637629 A	08-02-95	AU 6878094 A	16-02-95
		BR 9403153 A	11-04-95
		CA 2129399 A	05-02-95
		HU 67925 A	20-03-95
		NO 942886 A	06-02-95
		NZ 264113 A	25-06-96
		PL 304558 A	06-02-95
		PT 101556 A	04-05-95
		US 5599785 A	04-02-97
		US 5549840 A	27-08-96
		US 5610130 A	11-03-97
		ZA 9405565 A	29-01-96
EP 0125711 A	21-11-84	AU 555110 B	11-09-86
		AU 2683284 A	25-10-84
		CA 1219509 A	24-03-87
		JP 1610534 C	15-07-91
		JP 2032320 B	19-07-90
		JP 59223798 A	15-12-84
		US 4554099 A	19-11-85
WO 9405757 A	17-03-94	AU 4976193 A	29-03-94
		CA 2144065 A	17-03-94
		EP 0659205 A	28-06-95
		JP 8501120 T	06-02-96
		ZA 9306663 A	09-03-95

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PC1/US 97/04065

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5403515 A	04-04-95	AU 678360 B	29-05-97
		AU 4318493 A	04-01-94
		AU 678170 B	22-05-97
		AU 4708593 A	15-03-94
		CA 2143108 A	03-03-94
		CZ 9500492 A	12-07-95
		CZ 9403195 A	17-05-95
		DE 69302384 D	30-05-96
		DE 69302384 T	26-09-96
		DE 69310750 D	19-06-97
		WO 9325654 A	23-12-93
		WO 9404644 A	03-03-94
		EP 0647264 A	12-04-95
		EP 0656936 A	14-06-95
		ES 2087743 T	16-07-96
		HU 70082 A	28-09-95
		HU 71957 A	28-02-96
		JP 7507584 T	24-08-95
		JP 8500376 T	16-01-96
		PL 307685 A	12-06-95
		SK 24595 A	11-07-95
		SK 154894 A	11-07-95
		ZA 9305771 A	09-02-95
EP 0336878 A	11-10-89	AT 122383 T	15-05-95
		AU 2987489 A	10-08-89
		CA 1332338 A	11-10-94
		DE 68922522 D	14-06-95
		DE 68922522 T	14-09-95
		NO 174430 B	24-01-94
		PT 89679 B	29-04-94
		US 5192460 A	09-03-93
		US 5039441 A	13-08-91
		US 5294364 A	15-03-94